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NUCLEOTIDE CROSSLINKED POLYBUTADIENE FOR REPLACEMENT OF ISOCYANATE-CURED HYDROXYL-TERMINATED POLYBUTADIENE (HTPB) SYSTEMS

10 August 2014

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Outline



- Background / Motivation
 - Propellant binder history
 - Current solid propellant binder systems use polyurethane crosslinks from the reaction of hydroxyl-terminated polybutadiene (HTPB) with isocyanates
 - Isocyanates are known to cause respiratory irritation, occupational asthma and evidence of carcinogenic effects in animals.
 - OSHA currently considering further reductions in permissible exposure limits of isocyanates
- Objective
 - Replace isocyanate cure systems with crosslinking chemistries that are unlikely to pose health concerns now and in the future
 - Retention of key performance characteristics
 - $T_g < -40\text{ }^{\circ}\text{F}$
 - Tensile strength at $77\text{ }^{\circ}\text{F} > 100\text{ psi}$
 - Elongation at break at $77\text{ }^{\circ}\text{F} > 100\%$
 - Compatibility with $> 80\%$ salt and aluminum particles
- Approach
 - Biological model systems
 - Nucleobase binding (DNA)
 - Thiol-ene “click” chemistry (reaction of polythiols with alkenes)



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Propellant Binder History

- Chinese military rockets in 13th century – earliest use of solid propellants
- Mixture of loose powder containing sulfur, nitrate salts, carbon (charcoal)
 - Unreliable ballistic properties
 - Could not be used in large diameter, high thrust motors
- Consolidation of loose powders into solid forms (grains)
 - Solid mass that can be molded to conform to a wide range of motor geometries
 - Deliver long duration thrust in a programmed manner
 - Molten Asphalt
 - Heated to a fluid melt, mixed with oxidant, cast into motor cavity and allowed to cool
 - Low solids content which could be formulated
 - Poor mechanical properties of highly loaded asphalt
 - Acrylate monomers
 - Monomers mixed with oxidizers and curative (divinyl benzene)
 - Mixture cast then heated to cure temperature
 - Cure exotherm sometimes uncontrollable
 - Shrinkage of solid

Cohen, M.S., Advanced Binders for Solid Propellants - A Review. *Advanced Propellant Chemistry*. American Chemical Society, 1996 Ch.10, pp 93-107.

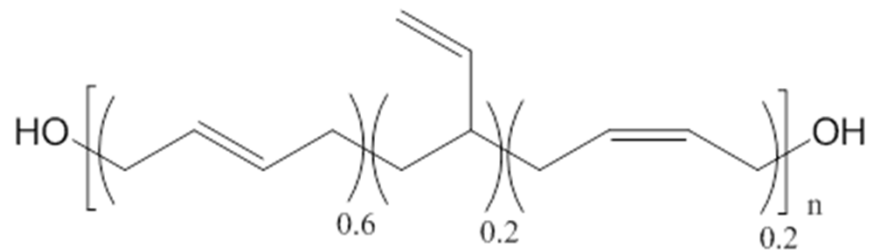


Propellant Binder History

- Consolidation of loose powders into solid forms (grains)
 - Partially polymerized liquids
 - Controlled molecular weight polymers of butadiene and acrylic acid
 - Cured with epoxy or imine
 - 80-85 percent solids – castable mix
 - Random crosslinks throughout chain
 - End functionalized polymers cured with trisimines
 - Nitro containing binders
 - Earliest solid binder was cellulose nitrate plasticized with nitroglycerin
 - Glycidyl nitrate
 - Petrin acrylate
 - Addition and condensation nitro polymers
 - Perchlorate group as an amine salt
 - Difluoroamino and fluorocarbon binders
 - Perchlorate group as an amine salt
 - Difluoroamino and fluorocarbon binders
 - Energetic binders



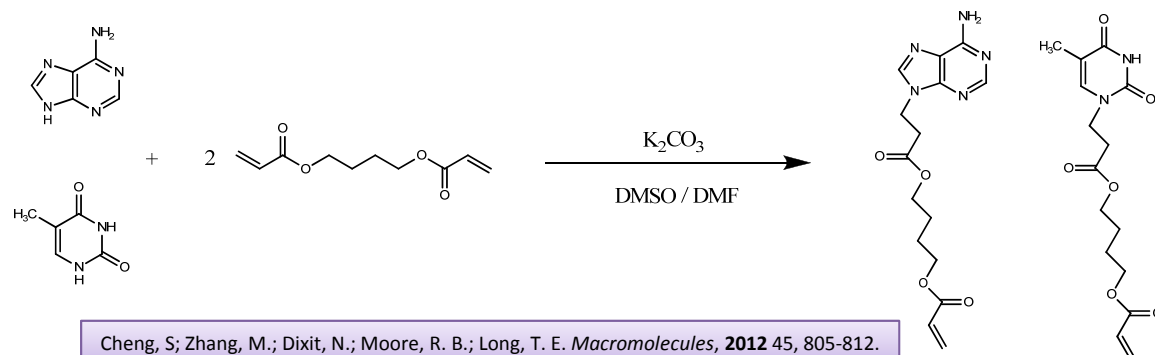
Isocyanate cured hydroxyl-terminated polybutadiene (HTPB) binders



- Three components in a binder (grain): polymeric binder, inorganic oxidizer and metallic fuel
- Polyurethane binder consists of
 - Polyol (HTPB)
 - Isocyanate curative
- Propellant grain characteristics
 - Sufficient tensile strength and elongation to handle thermal cycling, transportation and sudden pressurization on ignition
 - Maintain elasticity at low temperatures (Low T_g)
 - Compatibility with oxidizer and fuel
 - Maintain structural integrity with high solid content (~80 %)
- Free radical polymerized HTPB
 - Mixture of 1,4 and 1,2 addition
 - T_g -70 °C
 - Average of 2.5 OH groups per chain

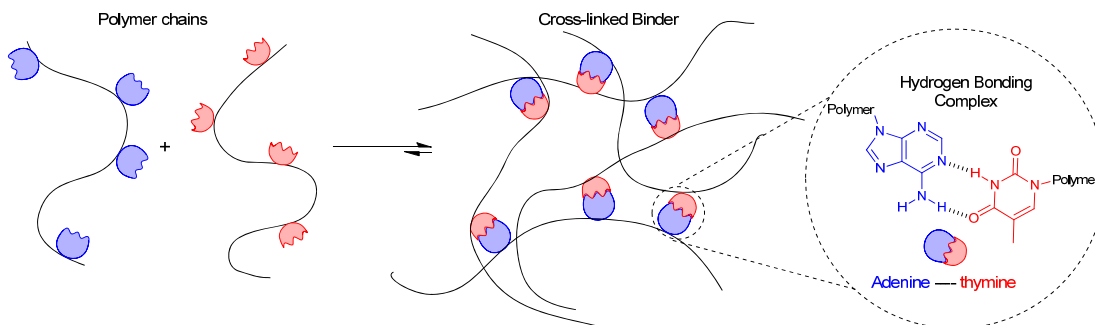
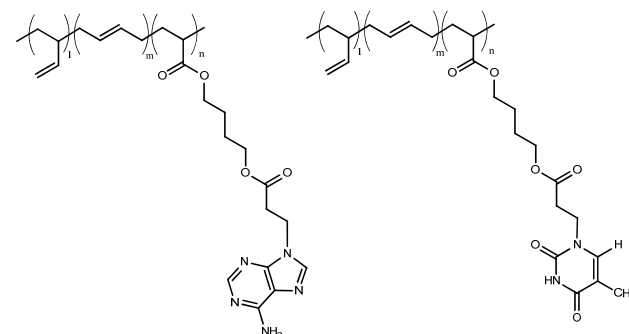
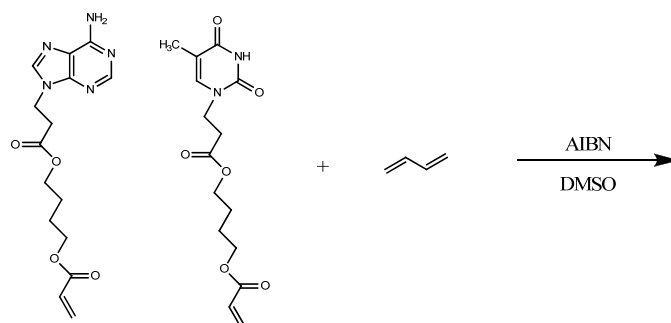


Incorporation of Nucleotide Bases in Polybutadiene



Adenine and thymine monomeric units were synthesized by Michael addition of a nucleobase with butanediol diacrylate. Incorporation of aliphatic spacer is expected to promote compatibility with HTPB and retention of desirable properties

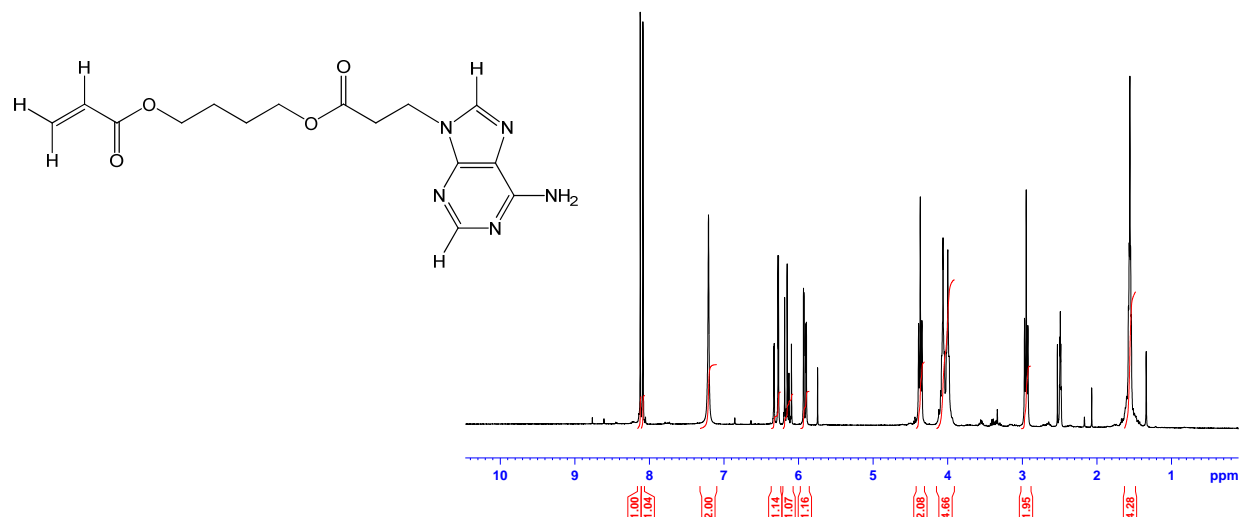
Copolymerization of either adenine or thymine methacrylate with butadiene gives an "A" and "B" complementary copolymers



When in the presence of each other complementary copolymers associate and form a crosslinked system consisting of hydrogen bonds

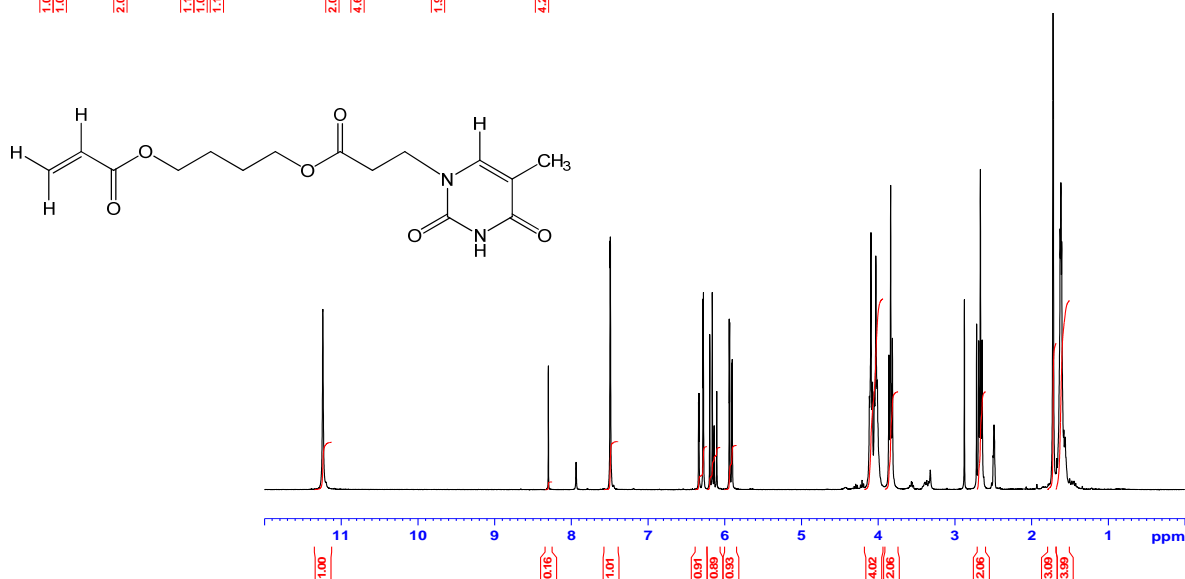


Adenine, Thymine Acrylate Characterization



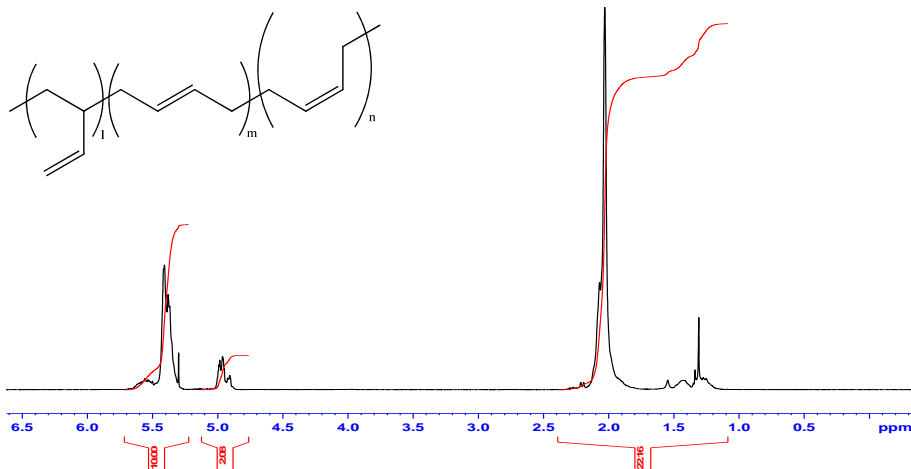
- N-9 substituted adenine acrylate was the major product. N-7 adduct and excess butanediol diacrylate was removed by flash chromatography
- NMR confirms N-7 addition
- Characteristic vinyl protons present with the expected integration

- N-1 substituted thymine acrylate was the major product.
- NMR confirms N-1 addition
- Characteristic vinyl protons present with the expected integration



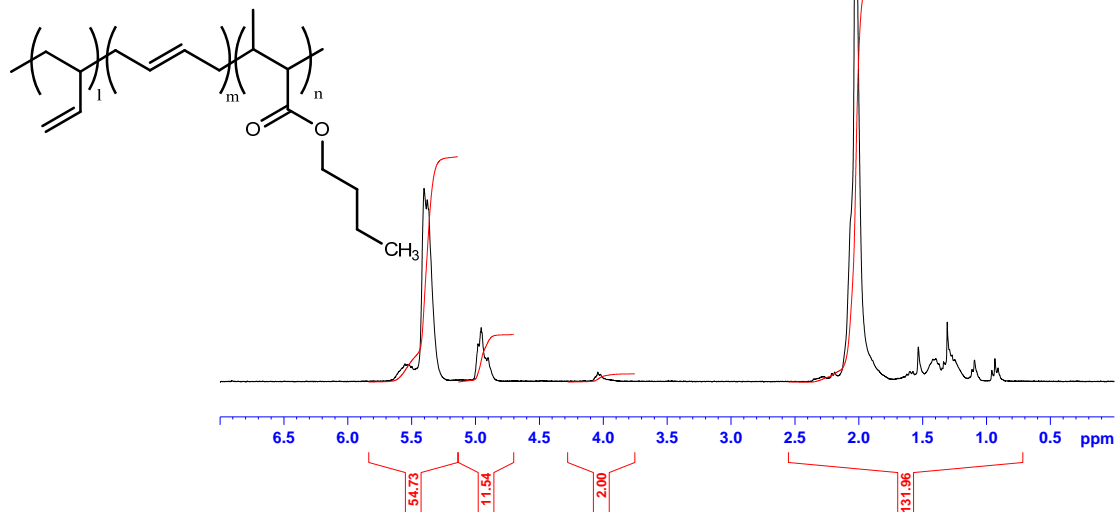


Butadiene Polymerization / Butyl Methacrylate Copolymerization



- Optimization of butadiene polymerization performed in toluene with AIBN as initiator
- Polymerization performed at 70 °C for 48 hours at approximately 2 atm
- Polybutadiene contained 20% 1,2 addition
- Overall yield of ~20% was obtained from multiple polymerizations

- Due to the low yield of butadiene polymerization, copolymerization of butadiene with butyl methacrylate was performed to estimate expected incorporation of nucleobase acrylate with a given feed ratio
- Copolymerization of butadiene with butyl methacrylate was performed in toluene with AIBN as initiator
- Butyl acrylate incorporation of 3.2 mol% was obtained from a 2 mol% feed ratio
- Overall yield of 22% was consistent with butadiene homopolymerizations

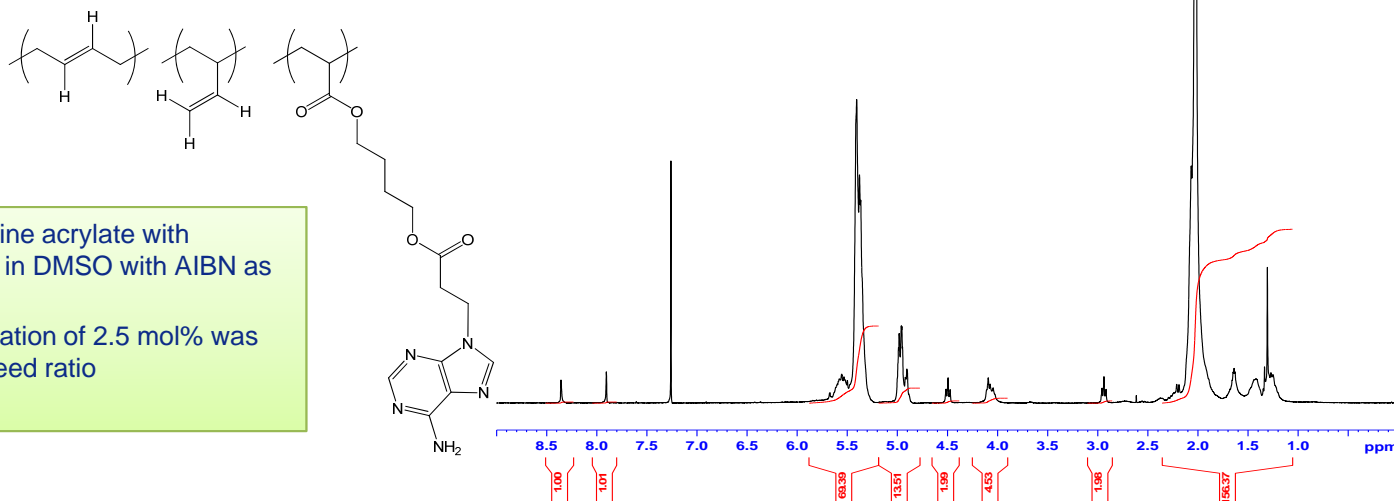




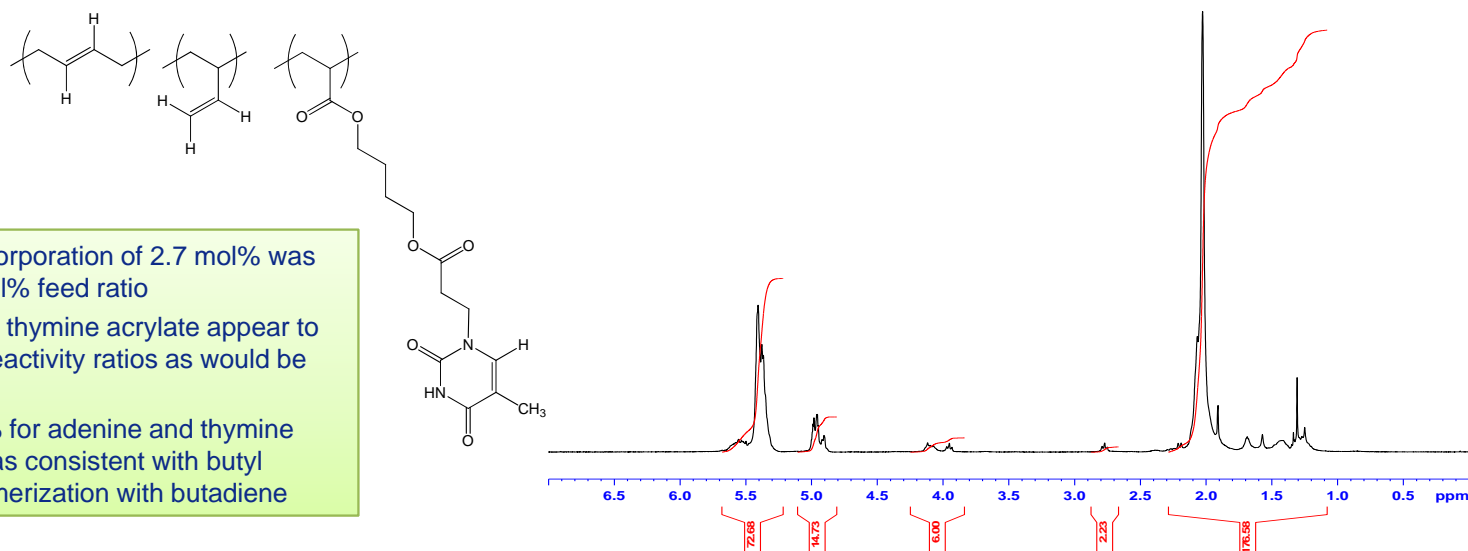
Adenine and Thymine Acrylate / Butadiene Copolymerization



- Copolymerization of adenine acrylate with butadiene was performed in DMSO with AIBN as the initiator
- Adenine acrylate incorporation of 2.5 mol% was obtained from a 4 mol% feed ratio



- Thymine acrylate incorporation of 2.7 mol% was obtained from a 4 mol% feed ratio
- Adenine acrylate and thymine acrylate appear to have near identical reactivity ratios as would be expected
- Overall yield of ~20% for adenine and thymine copolymerizations was consistent with butyl methacrylate copolymerization with butadiene

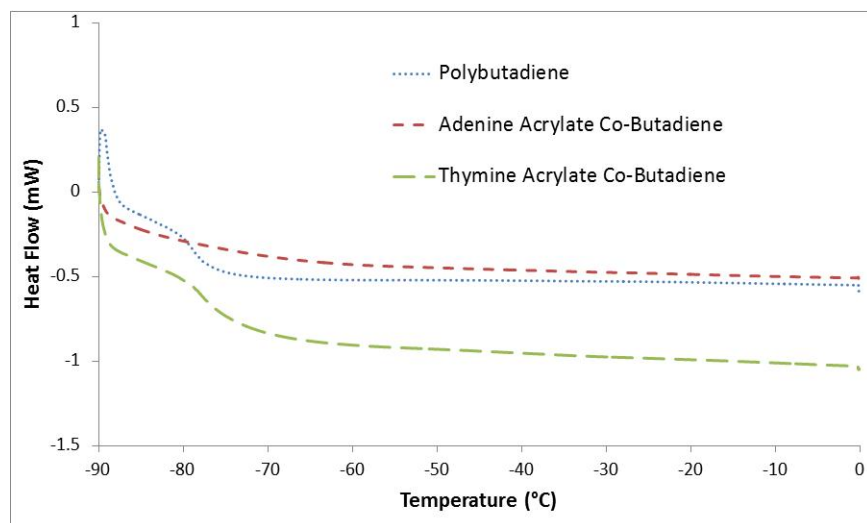




Nucleotide Copolymer T_g s

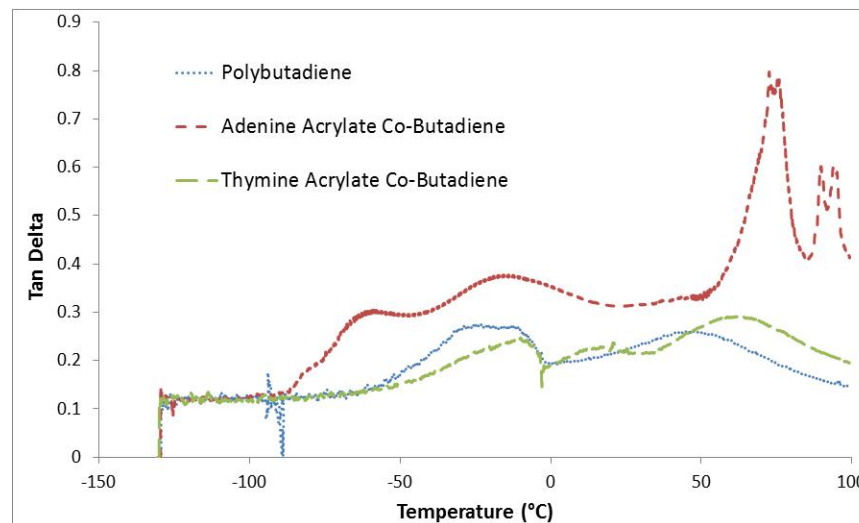


DSC



- Polybutadiene synthesized by free radical addition displayed a T_g (-79 °C) near that of commercial HTPB
- Incorporation of thymine acrylate in polybutadiene resulted in a small increase in T_g that suggests little self-association between thymine units with 2.5 mol% incorporation
- The single transition of thymine acrylate suggests that the nucleobase monomer is distributed randomly in the polymer backbone

TMA

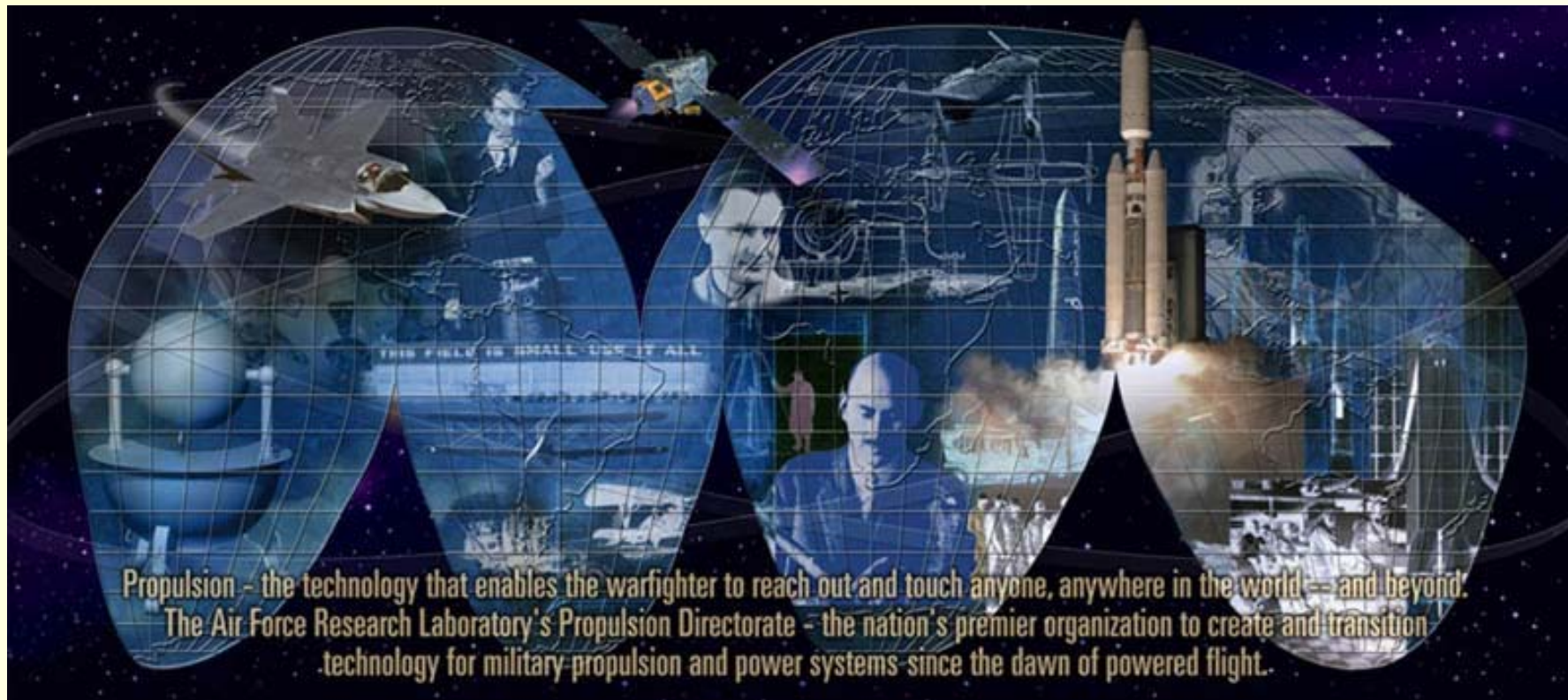


- Low temperature transitions are present in TMA tan delta that were not detected by DSC
- TMA indicated adenine acrylate has a T_g of -60 °C
- Incorporation of thymine acrylate in polybutadiene resulted in a small increase in T_g
- Multiple transitions seen in TMA may be due to self association between adenine units
- Adenine and thymine copolymers have nearly identical T_g s, as seen in DSC, but are both ~40 °C higher in TMA



Summary

- Acrylic nucleobase monomers were synthesized from the Michael addition of a nucleobase with butanediol diacrylate
- Copolymerization of nucleobase acrylates at a 4 mol% overall feed ratio with butadiene resulted in copolymers with ~2 mol% nucleobase incorporation and ~20% overall yield, consistent with butadiene homopolymerizations and butyl methacrylate / butadiene copolymerization
- Nearly identical nucleobase incorporation in butadiene suggests the two nucleobase monomeric units have identical reactivity ratios
- T_g of thymine acrylate copolymer, measured by both DSC and TMA, was nearly identical to that of polybutadiene
- T_g of adenine acrylate was not seen in DSC but was found to be -60 °C by TMA
- Secondary transitions above T_g were observed for the adenine copolymer in both DSC and TMA which may be due to self association of adenine units



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